# **APPENDIX G**

# STATISTICAL AND GEOCHEMICAL EVALUATION OF SITE METALS DATA

STATISTICAL (TIERS 1 AND 2)

# Statistical Comparison of Site and Background Data Range, Choccolocco Corridor, Parcel 143Q Fort McClellan, Alabama

#### 1.0 Introduction

This report provides the Tier 1 and Tier 2 site-to-background comparison results for the Range, Choccolocco Corridor, Parcel 143Q, at Fort McClellan in Calhoun County, Alabama. Tier 1 and Tier 2 evaluations (Shaw E & I, 2003) have been performed on the surface soil, subsurface soil, and groundwater data sets. In the first step of the comparison, the maximum detected concentration (MDC) of each element is compared to two times the arithmetic mean of the background data (SAIC, 1998). Any metal that has an MDC greater than the background screening value is carried forward for Tier 2 evaluation, which includes the Slippage Test, the Wilcoxon Rank Sum Test (WRS), and Hot Measurement Test.

The methodology and results of the Tier 1 and Tier 2 comparisons are summarized in Tables 1 through 3, and described in more detail in the following sections. Site samples used in the site-to-background comparison include 11 surface soil samples (0 to 1 foot below ground surface [bgs]), 8 subsurface soil samples (3 to 4 feet bgs), and 2 groundwater samples, that were collected at the site.

Background distributions and screening values have been established for target analyte list metals in surface soil, subsurface soil, and groundwater for Fort McClellan (SAIC, 1998).

# 2.0 Comparison Methodology

This section describes the statistical techniques that were employed in the Parcel 143Q site-to-background comparisons.

#### 2.1 Statistical Procedures

Contamination can be caused by a variety of processes that yield different spatial distributions of elevated contaminant concentrations. Slight but pervasive contamination can occur from non-point-source releases, and can result in slight increases in contaminant concentrations in a large percentage of samples. Localized, or "hot-spot," contamination can result in elevated concentrations in a small percentage of the total number of site samples. No single two-sample statistical comparison test is sensitive to both of these modes of contamination. For this reason, the use of several simultaneous tests is recommended for a valid and complete comparison of site

Table 1

Summary of Tier 1 and Tier 2 Site to Background Comparison for Surface Soil Range, Choccolocco Corridor, Parcel 143Q
Fort McClellan, Calhoun County, Alabama

	Frequency				Hot	Carried Forward
	of	Tier 1	Slippage	Wilcoxon Rank	Measurement	for Tier 3
Metals	Detection	Evaluation <sup>a</sup>	Test <sup>b</sup>	Sum Test <sup>b</sup>	Test <sup>b,c</sup>	Geochemical Evaluation
Aluminum	11 / 11	Failed	Passed	Failed	NA	Yes
Antimony	0 / 11	NA	NA	NA	NA	
Arsenic	11 / 11	Passed	NA	NA	NA	
Barium	11 / 11	Failed	Passed	Failed	NA	Yes
Beryllium	8 / 11	Failed	Passed	Failed	NA	Yes
Cadmium	0 / 11	NA	NA	NA	NA	
Calcium	11 / 11	Failed	Passed	Passed	NA	
Chromium	11 / 11	Passed	NA	NA	NA	
Cobalt	11 / 11	Passed	NA	NA	NA	
Copper	11 / 11	Passed	NA	NA	NA	
Iron	11 / 11	Passed	NA	NA	NA	
Lead	11 / 11	Failed	Passed	Failed	NA	Yes
Magnesium	11 / 11	Passed	NA	NA	NA	
Manganese	11 / 11	Failed	Passed	Failed	NA	Yes
Mercury	10 / 11	Failed	Passed	NA <sup>e</sup>	Passed	
Nickel	11 / 11	Failed	Passed	Failed	NA	Yes
Potassium	11 / 11	Failed	Passed	Failed	NA	Yes
Selenium	11 / 11	Failed	Failed	NA <sup>e</sup>	Failed	Yes
Silver	0 / 11	NA	NA	NA	NA	
Sodium	11 / 11	Passed	NA	NA	NA	
Thallium	0 / 11	NA	NA	NA	NA	
Vanadium	11 / 11	Passed	NA	NA	NA	
Zinc	11 / 11	Failed	Passed	Failed	NA	Yes

NA = not applicable; MDC = maximum detected concentration; UTL = upper tolerance limit

for FTMC Revision 2, Technical Memorandum, 24 June 2003 by Paul Goetchius.

a Tier 1 evaluation per Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments

b Part of Tier 2 evaluation per the above referenced memo.

c Performed only when the Slippage test and/or WRS test cannot be performed.

d Slippage test is not performed on data sets for which the maximum background value is a nondetect.

e WRS test is not performed on data sets containing 50% or more nondetects.

Table 2

Summary of Tier 1 and Tier 2 Site to Background Comparison for Subsurface Soil Range, Choccolocco Corridor, Parcel 143Q

Fort McClellan, Calhoun County, Alabama

	Frequency				Hot	Carried Forward
	of	Tier 1	Slippage	Wilcoxon Rank	Measurement	for Tier 3
Metals	Detection	Evaluation <sup>a</sup>	Test⁵	Sum Test <sup>b</sup>	Test <sup>b,c</sup>	Geochemical Evaluation
Aluminum	8 / 8	Failed	Failed	Failed	NA	Yes
Antimony	0 / 8	NA	NA	NA	NA	
Arsenic	8 / 8	Passed	NA	NA	NA	
Barium	8 / 8	Passed	NA	NA	NA	
Beryllium	5 / 8	Passed	NA	NA	NA	
Cadmium	0 / 8	NA	NA	NA	NA	
Calcium	8 / 8	Passed	NA	NA	NA	
Chromium	8 / 8	Failed	Passed	Failed	NA	Yes
Cobalt	7 / 8	Passed	NA	NA	NA	
Copper	8 / 8	Passed	NA	NA	NA	
Iron	8 / 8	Failed	Passed	Failed	NA	Yes
Lead	8 / 8	Failed	Passed	Failed	NA	Yes
Magnesium	8 / 8	Passed	NA	NA	NA	
Manganese	8 / 8	Failed	Passed	Failed	NA	Yes
Mercury	8 / 8	Failed	Failed	NA <sup>e</sup>	Failed	Yes
Nickel	8 / 8	Failed	Passed	Failed	NA	Yes
Potassium	8 / 8	Passed	NA	NA	NA	
Selenium	÷7 / 8	Failed	$NA^d$	NA <sup>e</sup>	Failed	Yes
Silver	1 / 8	Failed	$NA^d$	NA <sup>e</sup>	Failed	Yes
Sodium	7 / 8	Passed	NA	NA	NA	
Thallium	1 / 8	Passed	NA	NA	NA	
Vanadium	8 / 8	Failed	Passed	Failed	NA	Yes
Zinc	8 / 8	Failed	Passed	Failed	NA	Yes

NA = not applicable; MDC = maximum detected concentration; UTL = upper tolerance limit

for FTMC Revision 2, Technical Memorandum, 24 June 2003 by Paul Goetchius.

a Tier 1 evaluation per Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments

b Part of Tier 2 evaluation per the above referenced memo.

c Performed only when the Slippage test and/or WRS test cannot be performed.

d Slippage test is not performed on data sets for which the maximum background value is a nondetect.

e WRS test is not performed on data sets containing 50% or more nondetects.

Table 3

Summary of Tier 1 and Tier 2 Site to Background Comparison for Goundwater Range, Choccolocco Corridor, Parcel 143Q

Fort McClellan, Calhoun County, Alabama

	Frequency				Hot	Carried Forward
	of	Tier 1	Slippage	Wilcoxon Rank	Measurement	for Tier 3
Metals	Detection	Evaluation <sup>a</sup>	Test <sup>b</sup>	Sum Test <sup>b</sup>	Test <sup>b,c</sup>	Geochemical Evaluation
Aluminum	2 / 2	Passed	NA	NA	NA	
Antimony	0 / 2	Passed	NA	NA	NA	
Arsenic	1 / 2	Passed	NA	NA	NA	
Barium	2 / 2	Passed	NA	NA	NA	
Beryllium	0 / 2	Passed	NA	NA	NA	
Cadmium	0 / 2	Passed	NA	NA	NA	
Calcium	2 / 2	Passed	NA	NA	NA	
Chromium	0 / 2	Passed	NA	NA	NA	
Cobalt	1 / 2	Passed	NA	NA	NA	
Copper	0 / 2	Passed	NA	NA	NA	
Iron	2 / 2	Passed	NA	NA	NA	
Lead	0 / 2	Passed	NA	NA	NA	
Magnesium	2/2	Passed	NA	NA	NA	
Manganese	2/2	Passed	NA	NA	NA	
Mercury	0 / 2	Passed	NA	NA	NA	
Nickel	0 / 2	Passed	NA	NA	NA	
Potassium	2 / 2	Passed	NA	NA	NA	
Selenium	2 / 2	Failed	$NA^d$	NA <sup>e</sup>	Passed	
Silver	0 / 2	Passed	NA	NA	NA	
Sodium	2/2	Passed	NA	NA	NA	
Thallium	0 / 2	Passed	NA	NA	NA	
Vanadium	0 / 2	Passed	NA	NA	NA	
Zinc	0 / 2	Passed	NA	NA	NA	

NA = not applicable; MDC = maximum detected concentration; UTL = upper tolerance limit

for FTMC Revision 2, Technical Memorandum, 24 June 2003 by Paul Goetchius.

a Tier 1 evaluation per Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments

b Part of Tier 2 evaluation per the above referenced memo.

c Performed only when the Slippage test and/or WRS test cannot be performed.

d Slippage test is not performed on data sets for which the maximum background value is a nondetect.

e WRS test is not performed on data sets containing 50% or more nondetects; or when the sample size is less than 5.

versus background distributions (U.S. Environmental Protection Agency [EPA], 1989, 1992, and 1994; U.S. Navy, 2002).

Analytes that fail the Tier 1 and Tier 2 comparisons are subject to a geochemical evaluation to determine if the elevated concentrations are due to natural processes or if they represent potential contamination.

**2.1.1 Tier 1 -** In this step of the background screening process, the maximum detected concentration (MDC) of the site data set is compared to the background screening value of two times the background mean (SAIC, 1998). Elements for which the site MDC does not exceed the background screening value are considered to be present at background concentrations, and are not considered site-related chemicals. Elements for which the site MDC exceeds the background screening value undergo further evaluation (Tier 2).

#### 2.1.2 Tier 2 -

Slippage Test – The nonparametric Slippage test is designed to detect a difference between the upper tails of two distributions, and has been recommended for use in site-to-background comparisons to identify potential localized, or hot-spot, contamination (U.S. Navy, 2002). The test is performed by counting the number (K) of detected concentrations in the site data set that exceed the maximum background measurement, and then comparing this number to a critical value  $(K_c)$ , which is a function of the number of background samples and the number of site samples. If  $K > K_c$ , then potential contamination is indicated and the analyte will be subjected to geochemical evaluation. If  $K \le K_c$ , then localized contamination is not suspected.

Critical values tables for site and background data sets up to size n = 50 are provided in U.S. Navy (2002). Critical values for larger data sets are calculated using the test statistic provided in Rosenbaum (1954). In this report, the Slippage test is performed at the 95 percent confidence level. The test cannot be performed if the maximum background value is a nondetect, because the actual concentration in that sample is unknown.

Wilcoxon Rank Sum Test. The nonparametric WRS test is designed to detect a difference between the medians of two data sets, and has been recommended for use in site-to-background comparisons to identify slight but pervasive contamination (EPA, 2000; U.S. Navy, 2002). In this report, the WRS test is performed when the site and background data sets each contain less than 50 percent nondetects (i.e., measurements reported as not detected below the laboratory reporting limit). The WRS test will not be performed on data sets containing 50 percent or more

nondetects. The medians of such data sets are unknown, and hence the test results would lack sufficient power to yield reliable results.

The WRS test compares two data sets of size n and m (n > m), and tests the null hypothesis that the samples were drawn from populations with distributions having the same medians. To perform the test, the two sets of observations are pooled and arranged in order from smallest to largest. Each observation is assigned a rank; that is, the smallest is ranked 1, the next largest is ranked 2, and so on up to the largest observation, which is ranked (n + m). If ties occur between or within samples, each one is assigned the mid-rank. Next, the sum of the ranks of smaller data set m is calculated. Then the test statistic Z is determined,

$$Z = \frac{W - m(m+n+1)/2}{\sqrt{mn(m+n+1)/12}}$$

Where:

W = Sum of the ranks of the smaller data set

m =Number of data points in smaller group

n =Number of data points in larger group.

This test statistic Z is used to find the two-sided significance. For instance, if the test statistic yields a probability of a Type I error (p-level) less than 0.2, then there is a statistically significant difference between the medians at the 80 percent confidence level. A Type I error involves rejecting the null hypothesis when it is true. If the p-level is greater than 0.2, then there is no reasonable justification to reject the null hypothesis at the 80 percent confidence level. It can therefore be concluded that the medians of the two data sets are similar, and it can be assumed to be drawn from the same population.

If the p-level is less than 0.2, then the medians of the two distributions are significantly different at the 80 percent confidence level. This can occur if the site data are shifted higher or lower than the background data. If the site data are shifted higher relative to background, then contamination may be indicated, and the analyte in question will be carried on for geochemical evaluation; however, if the site data are shifted lower relative to background, then contamination is not indicated. If the p-level is greater than 0.2, then pervasive site contamination is not suspected.

**Box Plots.** A quick, robust graphical method recommended by the EPA to visualize and compare two or more groups of data is the box plot comparison (EPA, 1989 and 1992). These plots provide a summary view of the entire data set, including the overall location and degree of symmetry. The box encloses the central 50 percent of the data points so that the top of the box represents the 75<sup>th</sup> percentile and the bottom of the box represents the 25<sup>th</sup> percentile. The small box within the larger box represents the median of the data set. The upper whisker extends outward from the box to the maximum point and the lower whisker extends to the minimum point. Nondetect results are set equal to one-half of the reporting limit for plotting purposes.

For each analyte, box plots of site and background data are placed side by side to visually compare the distributions and qualitatively determine whether the data sets are similar or distinct. Accordingly, the box plots are a necessary adjunct to the WRS test. As described previously, the WRS test may indicate that the medians of the site and background data sets are significantly different. Examination of the box plots will confirm whether that difference is caused by site data that are shifted higher or lower relative to background.

Hot Measurement Test. The hot measurement test consists of comparing each site measurement with a concentration value that is representative of the upper limit of the background distribution (EPA, 1994). Ideally, a site sample with a concentration above the background screening value would have a low probability of being a member of the background distribution, and may be an indicator of contamination. It is important to select such a background screening value carefully so that the probability of falsely identifying site samples as contaminated or uncontaminated is minimized.

The 95<sup>th</sup> upper tolerance limit (95<sup>th</sup> UTL) is recommended as a screening value for normally or lognormally distributed analytes and the 95<sup>th</sup> percentile is recommended as a screening value for nonparametrically distributed analytes (EPA, 1989, 1992, and 1994). Site samples with concentrations above these values are not necessarily contaminated, but should be considered suspect. To perform the test, each analyte's site MDC is compared to the background 95<sup>th</sup> UTL or 95<sup>th</sup> percentile, in accordance with the type of background distribution. If the site MDC exceeds the background screening value, then that analyte will undergo a geochemical evaluation. If the MDC does not exceed the background threshold value, then hot-spot contamination is not indicated.

#### 2.1.3 Geochemical Evaluation

If an analyte fails either of the statistical tests described above then a geochemical evaluation is performed to determine if the elevated concentrations are caused by natural processes. The methodology and results of the geochemical evaluation are provided separately.

# 3.0 Results of the Site-to-Background Comparisons

This section presents the results of the site-to-background comparisons for 23 TAL metals in the Parcel 143Q surface soil, subsurface soil, and groundwater samples. The WRS test results with corresponding box plots are provided in Attachment 1. Tables 1 through 3 summarize the Tier 1 and Tier 2 test results for each media as discussed in the following sections.

#### 3.1 Surface Soil

Twenty-three TAL metals were evaluated in the Parcel 143Q surface soil. Four metals (antimony, cadmium, silver, and thallium) had no detected concentrations in surface soil. No further discussion of these metals is included. In addition, eight metals, (arsenic, chromium, cobalt, copper, iron, magnesium, sodium, and vanadium) have MDCs less than their respective background screening values. Because they all passed the Tier 1 evaluation, they will not be discussed any further.

Table 1 summarizes the surface soil statistical site to background comparison results. The remaining eleven metals underwent the Tier 2 evaluation. The statistical test results are discussed in detail in the following section. Box plots are provided in Attachment 1.

#### Aluminum

#### Tier 1 Evaluation

Four site samples of aluminum exceed the background screening value of 16,306 mg/kg.

#### Slippage Test

The critical value,  $K_c$ , is 2. No site samples of aluminum exceed the maximum background measurement (K = 0). Because  $K < K_c$ , aluminum passes the Slippage test.

#### **WRS** Test

The p-level of < 0.001 indicates a significant difference between the site and background distributions.

#### **Box Plot**

The box plots visualize that the site minimum and interquartile range is higher than the corresponding background values (Figure 1-1).

#### Conclusion

Because aluminum in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

#### **Barium**

#### Tier 1 Evaluation

Two site samples exceed the background screening value of 123.94 mg/kg.

#### Slippage Test

 $K_c$  is 2, and no site samples of barium exceed the maximum background measurement. Because  $K < K_c$ , barium passes the Slippage test.

#### **WRS** Test

The p-level of 0.0017 indicates significant difference between the site and background distributions.

#### **Box Plot**

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-1).

#### Conclusion

Because barium in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

# Beryllium

#### Tier 1 Evaluation

Two site samples exceed the background screening value of 0.8 mg/kg.

#### Slippage Test

 $K_c$  is 2, and one site sample exceeds the maximum background measurement. Because  $K \le K_c$ , beryllium passes the Slippage test.

#### WRS Test

The p-level of 0.0012 indicates a significant difference between the site and background distributions.

#### **Box Plot**

The site minimum, interquartile range, and maximum are higher than the corresponding background values (Figure 1-2).

#### Conclusion

Because beryllium in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

#### Calcium

#### Tier 1 Evaluation

One site sample exceeds the background screening value of 1,723 mg/kg.

#### Slippage Test

The critical value,  $K_c$ , for calcium is 2, and no site samples exceed the maximum background measurement. Because  $K < K_c$ , calcium passes the Slippage test.

#### WRS Test

The p-level of 0.818 indicates excellent agreement between the site and background distributions.

#### **Box Plot**

The site median, 75<sup>th</sup> percentile and maximum are less than the respective background values (Figure 1-2).

#### Conclusion

Calcium in surface soil is considered within the range of background.

#### Lead

# Tier 1 Evaluation

One site sample exceeds the background screening value of 40.05 mg/kg.

#### Slippage Test

 $K_c$ , for lead is 2, and no site samples exceed the maximum background measurement. Because  $K_c$ , lead passes the Slippage test.

#### **WRS** Test

The p-level of 0.17 indicates weak agreement between the site and background distributions.

#### **Box Plot**

The site minimum, 25<sup>th</sup> percentile and median are higher than the respective background values (Figure 1-3).

#### Conclusion

Because lead in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

#### Manganese

#### Tier 1 Evaluation

Two site samples exceed the background screening value of 1,579 mg/kg.

# Slippage Test

 $K_c$  for manganese is 2, and no site samples exceed the maximum background measurement. Because  $K \le K_c$ , manganese passes the Slippage test.

The p-level of 0.01 indicates significant difference between the site and background distributions.

#### **Box Plot**

The site minimum and interquartile range are visibly higher with respect to background (Figure 1-3).

#### Conclusion

Because manganese in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

# Mercury

#### Tier 1 Evaluation

Three site samples exceed the background screening value of 0.08 mg/kg.

#### Slippage Test

The critical value for mercury,  $K_{c_s}$  is 2, and no site samples exceed the maximum background measurement. Since  $K < K_c$ , mercury passes the Slippage test.

#### **WRS** Test

The WRS test was not performed because the background data set contains more than 50 percent nondetects.

#### **Box Plot**

The site minimum and interquartile range are somewhat higher than the corresponding background values (Figure 1-4). The shape and location of the background box plot reflects the high percentage of nondetects (66 percent), and the replacement values of one-half the reporting limit.

#### Hot Measurement Test

No site samples of mercury exceed the background 95<sup>th</sup> percentile of 0.125 mg/kg.

#### Conclusion

Mercury in surface soil is considered within the range of background.

#### **Nickel**

#### Tier 1 Evaluation

Two site samples exceed the background screening value of 10.33 mg/kg.

#### Slippage Test

 $K_c$  for nickel is 2, and no site samples exceed the maximum background measurement. Because  $K < K_c$ , nickel passes the Slippage test.

The p-level of 0.005 indicates significant difference between the site and background distributions.

#### **Box Plot**

The site minimum and interquartile range are visibly higher with respect to the corresponding background values (Figure 1-4).

#### Conclusion

Because nickel in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

#### **Potassium**

#### Tier 1 Evaluation

One site sample exceeds the background screening value of 799.76 mg/kg.

#### Slippage Test

 $K_c$  for potassium is 2, and no site samples exceed the maximum background measurement. Because  $K \le K_c$ , potassium passes the Slippage test.

#### **WRS** Test

The p-level of < 0.001 indicates a significant difference between the site and background distributions.

#### **Box Plot**

The site minimum and interquartile range are visibly higher with respect to the corresponding background (Figure 1-5).

#### Conclusion

Because potassium in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

#### Selenium

#### Tier 1 Evaluation

Eleven detected concentrations in the site data set exceed the background screening value of 0.48 mg/kg.

#### Slippage Test

 $K_c$  for selenium is 2, and six site samples exceed the maximum background measurement. Because  $K > K_c$ , selenium fails the Slippage test.

#### WRS Test

No WRS test was performed because the background data set contains more than 50 percent nondetects.

#### **Box Plot**

The site minimum, interquartile range, and maximum are all above the corresponding background values (Figure 1-5). The shape and location of the background box plot reflect the high percentage of nondetects (99 percent), and the replacement values of one-half the reporting limit.

#### Hot Measurement Test

The site MDC exceeded the background 95<sup>th</sup> percentile of 0.563 mg/kg.

#### Conclusion

Because selenium in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

#### Zinc

#### Tier 1 Evaluation

One site sample exceeds the background screening value of 40.64 mg/kg.

#### Slippage Test

 $K_c$  for zinc is 2, and no site samples exceed the maximum background measurement. Because  $K_c$ , zinc passes the Slippage test.

#### **WRS** Test

The p-level of 0.047 indicates a significant difference between the site and background distributions.

#### **Box Plot**

The site minimum and interquartile range are higher than the respective background values (Figure 1-6).

#### Conclusion

Because zinc in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

#### 3.2 Subsurface Soil

Twenty-three TAL metals were evaluated in the Parcel 143Q subsurface soil. Two metals, antimony and cadmium, had no detected concentrations in subsurface soil so no further discussion of these metals is included. In addition, ten metals, (arsenic, barium, beryllium, calcium, cobalt, copper, magnesium, potassium, sodium, and thallium) have MDCs less than their respective background screening values. Because these metals passed the Tier 1 evaluation, they will not be discussed further.

Table 2 summarizes the subsurface soil statistical site to background comparison results. The remaining eleven metals underwent Tier 2 evaluation, and the test results are discussed below in detail. Box plots are provided in Attachment 1.

#### **Aluminum**

#### Tier 1 Evaluation

Five site samples of aluminum exceed the background screening value of 13,591 mg/kg.

#### Slippage Test

The critical value,  $K_c$ , of aluminum is 2. Four site samples exceed the maximum background measurement (K = 4). Because  $K > K_c$ , aluminum fails the Slippage test.

#### WRS Test

The p-level of < 0.001 indicates a significant difference between the site and background distributions.

#### **Box Plot**

The site minimum, interquartile range, and maximum are higher than the corresponding background values (Figure 1-6).

#### Conclusion

Because aluminum in subsurface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

#### Chromium

#### Tier 1 Evaluation

Three site samples of chromium exceed the background screening value of 38.25 mg/kg.

# Slippage Test

 $K_c$  for chromium is 2, and one site sample exceeds the maximum background measurement. Because  $K < K_c$ , chromium passes the Slippage test.

#### **WRS** Test

The p-level of 0.025 indicates a difference in the site and background distributions.

#### **Box Plot**

The site minimum, interquartile range, and maximum are higher than the corresponding background values (Figure 1-7).

#### Conclusion

Because chromium in subsurface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

#### Iron

#### Tier 1 Evaluation

One site sample exceeds the background screening value of 44,817 mg/kg.

# Slippage Test

 $K_c$  for iron is 2, and one site sample exceeds the maximum background measurement. Because  $K < K_c$ , iron passes the Slippage test.

#### **WRS** Test

The p-level of 0.043 indicates significant difference between the site and background distributions.

#### **Box Plot**

The site minimum and interquartile range are higher than the respective background values (Figure 1-7). The site and background maximums are similar.

#### Conclusion

Because iron in subsurface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

#### Lead

#### Tier 1 Evaluation

One site sample exceeds the background screening value of 38.53 mg/kg.

#### Slippage Test

 $K_c$  for lead is 2, and no site samples exceed the maximum background measurement. Because  $K_c$ , lead passes the Slippage test.

#### WRS Test

The p-level of 0.026 indicates a difference between the site and background distributions.

#### **Box Plot**

The site minimum and interquartile range are higher than the respective background values (Figure 1-8).

#### Conclusion

Because lead in subsurface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

# Manganese

#### Tier 1 Evaluation

One site samples exceeds the background screening value of 1355 mg/kg.

# Slippage Test

 $K_c$  for manganese is 2, and no site samples exceed the maximum background measurement. Because  $K \le K_c$ , manganese passes the Slippage test.

The p-level < 0.0302 indicates significant difference between the site and background distributions.

#### **Box Plot**

The site minimum and interquartile range are visibly higher with respect to background (Figure 1-8).

#### Conclusion

Because manganese in subsurface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

# Mercury

#### Tier 1 Evaluation

Eight site samples exceed the background screening value of 0.07 mg/kg.

#### Slippage Test

The critical value for mercury,  $K_c$ , is 2, and five site samples exceed the maximum background measurement. Since  $K > K_c$ , mercury fails the Slippage test.

#### **WRS** Test

The WRS test was not performed because the background data set contains more than 50 percent nondetects.

#### **Box Plot**

The site minimum, interquartile range, and maximum are elevated relative to the corresponding background values (Figure 1-9). The shape and location of the background box plot is influenced by the percentage of nondetects (53 percent), and the replacement values of one-half the reporting limit rather than detected concentrations.

#### Hot Measurement Test

The site MDC of mercury exceeds the background 95<sup>th</sup> percentile of 0.094 mg/kg.

#### Conclusion

Because mercury in subsurface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

# **Nickel**

#### Tier 1 Evaluation

One site sample exceeds the background screening value of 12.89 mg/kg.

#### Slippage Test

 $K_c$  for nickel is 2, and no site samples exceed the maximum background measurement. Because  $K < K_c$ , nickel passes the Slippage test.

The p-level of 0.0166 indicates a significant difference between the site and background distributions.

#### **Box Plot**

The site minimum and interquartile range are visibly higher than the respective background values (Figure 1-9).

#### Conclusion

Because nickel in subsurface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

#### Selenium

#### Tier 1 Evaluation

Seven detected concentrations in the site data set exceed the background screening value of 0.47 mg/kg.

#### Slippage Test

The maximum value in background is a nondetect, so the Slippage test could not be performed for selenium.

#### **WRS** Test

No WRS test was performed because the background data set contains greater than 50 percent nondetects.

#### **Box Plot**

The site minimum, interquartile range, and maximum are higher than the corresponding background values (Figure 1-10). The shape and location of the background box plot reflects the high percentage of nondetects (98 percent), and the replacement values of one-half the reporting limit.

#### Hot Measurement Test

The site MDC exceeds the background 95<sup>th</sup> percentile of 0.574 mg/kg.

#### Conclusion

Because selenium in subsurface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

#### Silver

#### Tier 1 Evaluation

One site sample exceeds the background screening value of 0.24 mg/kg.

# Slippage Test

The maximum background result is a nondetect, so the Slippage test cannot be performed.

No WRS test was performed because the site data set contains more than 50 percent nondetects.

#### Box Plot

The site minimum, interquartile range, and maximum are higher than the corresponding background values (Figure 1-10). The shape and location of the site box plot reflects the high percentage of nondetects (87 percent), and the replacement values of one-half the reporting limit rather than detected concentrations.

#### Hot Measurement Test

The site MDC exceeds the background 95<sup>th</sup> percentile of 0.88 mg/kg.

#### Conclusion

Because silver in subsurface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

#### Vanadium

# Tier 1 Evaluation

One site samples exceeds the background screening value of 64.89 mg/kg.

#### Slippage Test

 $K_c$  for vanadium is 2, and no site samples exceed the maximum background measurement. Because  $K \le K_c$ , vanadium passes the Slippage test.

#### **WRS** Test

The p-level of 0.063 indicates a weak agreement between the site and background distributions.

#### **Box Plot**

The site minimum and interquartile range are visibly higher than the respective background values (Figure 1-11).

#### Conclusion

Because vanadium in subsurface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

#### Zinc

#### Tier 1 Evaluation

One site sample exceeds the background screening value of 34.86 mg/kg.

#### Slippage Test

 $K_c$  for zinc is 2, and no site samples exceed the maximum background measurement. Because K <  $K_c$ , zinc passes the Slippage test.

#### **WRS** Test

The p-level of 0.06 indicates a weak agreement between the site and background distributions.

#### Box Plot

The site minimum and interquartile range are visibly higher than the respective background values (Figure 1-11).

#### Conclusion

Because zinc in subsurface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

# 3.3 Groundwater

This section presents the results of the site-to-background comparisons for 23 metals unfiltered groundwater samples. Twelve metals (antimony, beryllium, cadmium, chromium, copper, lead, mercury, nickel, silver, thallium, vanadium, and zinc) had no detects in the groundwater site samples and are not considered any further. Ten metals (aluminum, arsenic, barium, calcium, cobalt, iron, magnesium, manganese, potassium, and sodium) passed the Tier 1 evaluation, they had no detected concentrations exceeding their respective background screening values. These metals are considered within the range of background based on the Tier 1 evaluation, and will not be tested or discussed further. Table 2 summarizes these results.

Selenium is the remaining metal with detected concentrations exceeding the background screening value and is carried forward for Tier 2 evaluation. The results of this evaluation are summarized in Table 3 and discussed in detail below. The box plot is provided in Attachment 1.

#### Selenium

#### Tier 1 Evaluation

Selenium has no background screening value and there are two detected concentrations in the site samples.

#### Slippage Test

The maximum background result is a nondetect, so the Slippage test cannot be done.

#### **WRS** Test

Because the background data has more than 50 percent nondetects, and the site data set has less than 5 samples, the WRS test was not performed.

#### **Box Plot**

The site minimum, interquartile range, and maximum are elevated as compared to the corresponding background values (Figure 1-12). The shape and location of the background box plot reflects the high percentage of nondetects (100 percent), and the replacement values of one-half the reporting limit. The box plot for the site data reflects the insufficient sample size (n=2).

#### Hot Measurement Test

The site MDC is less than the background 95<sup>th</sup> percentile of 0.0971 mg/L.

#### Conclusion

Based on the Hot Measurement test, selenium is considered within the range of background.

# 4.0 Summary and Conclusions

The statistical methodology used to compare the Parcel 143Q and background data sets for 23 elements in surface soil, subsurface soil, and groundwater includes a comparison of the site MDC to the background screening value, Tier 1 evaluation. Analytes that failed this comparison were subjected to the Slippage test and WRS test. Box-and-whisker plots were prepared to visually compare the two data sets and properly interpret the WRS test results. For elements with data sets that did not allow for either the Slippage test or WRS test to be performed, the Hot Measurement test was used. Analytes that failed these statistical tests, Tier 2 evaluation, are carried forward for Tier 3 geochemical evaluation to determine if natural processes can explain the elevated concentrations.

Tables 1 through 3 summarize the comparison test results for surface soil, subsurface soil, and groundwater respectively. The summary tables also show those metals that must be carried forward for Tier 3 geochemical evaluation.

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Figure 1-1

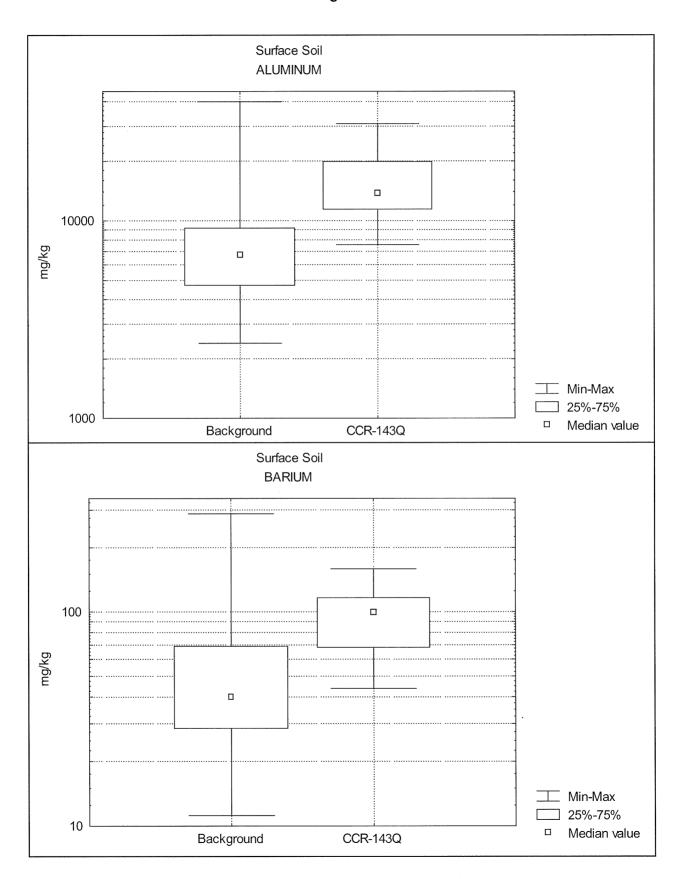


Figure 1-2

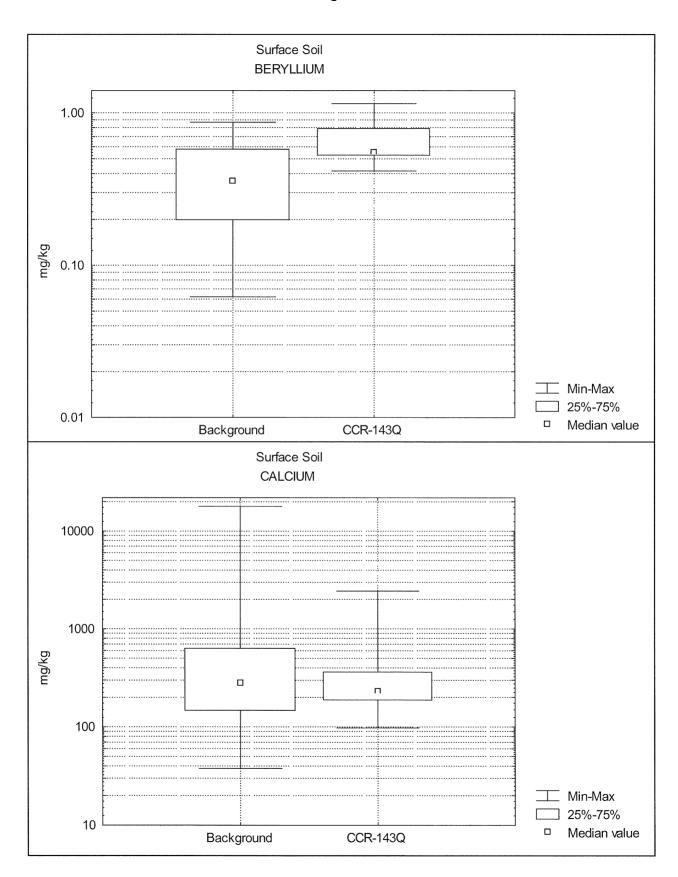


Figure 1-3

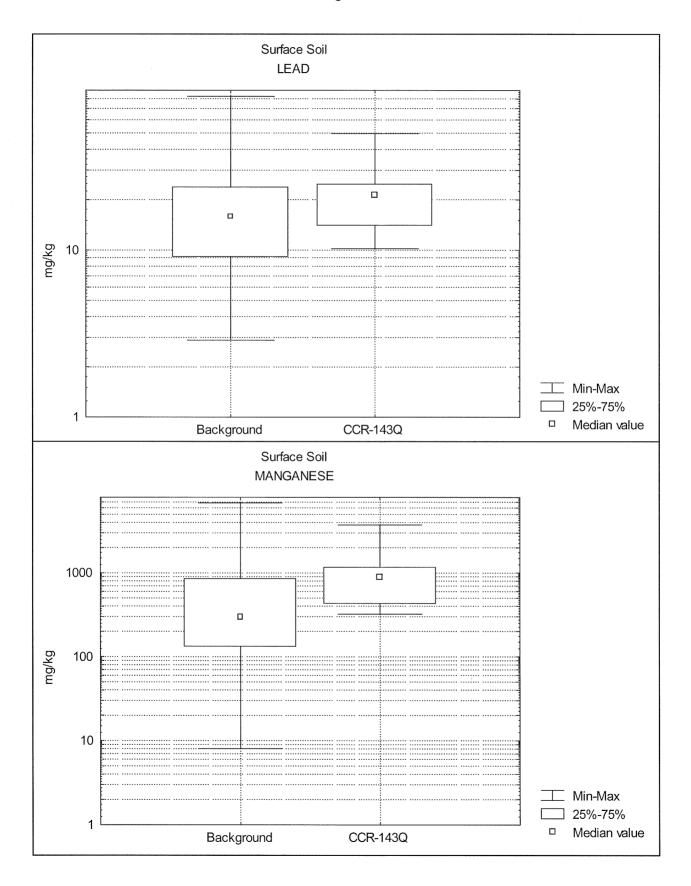


Figure 1-4

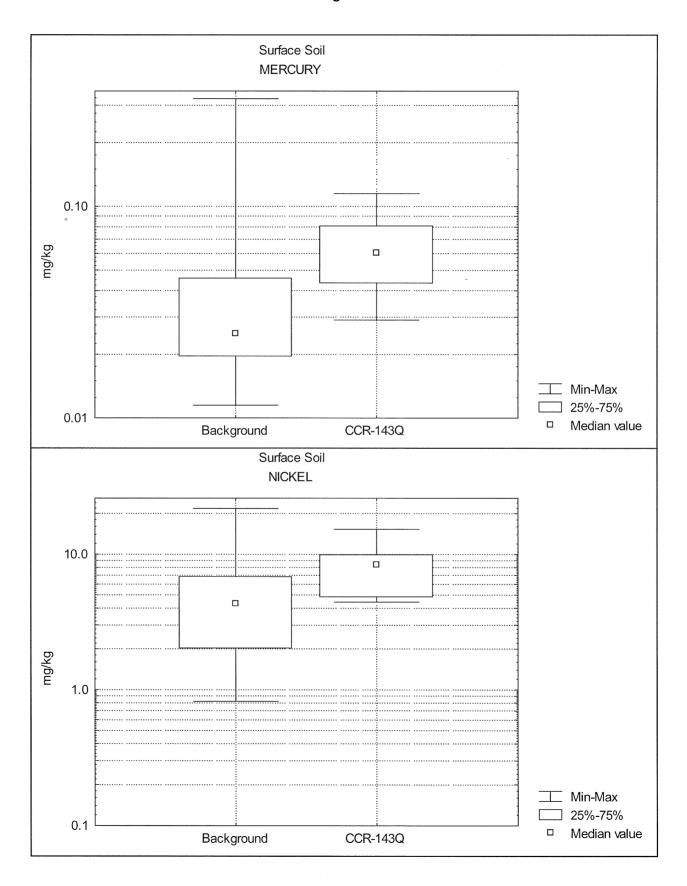


Figure 1-5

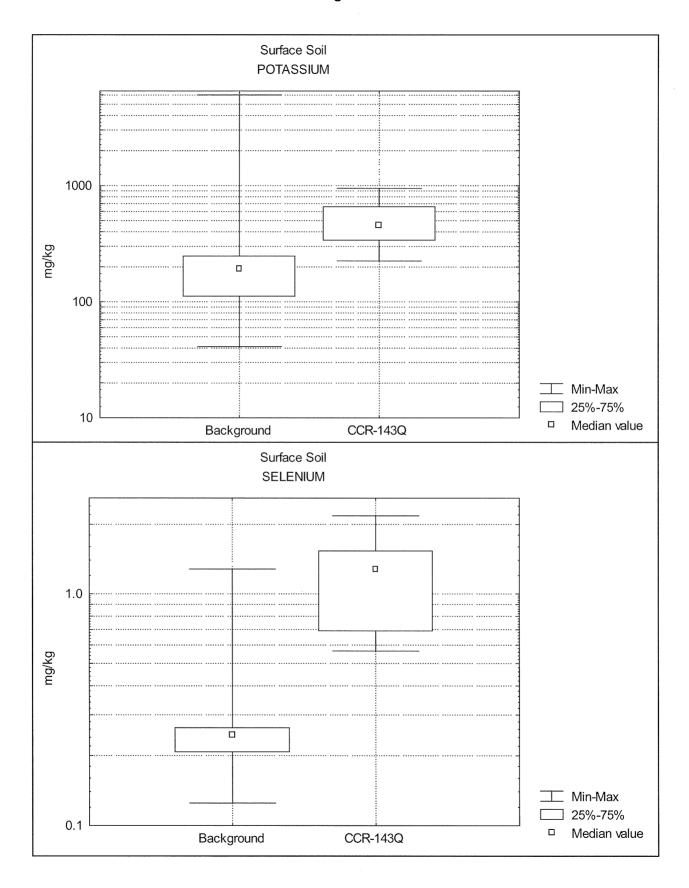


Figure 1-6

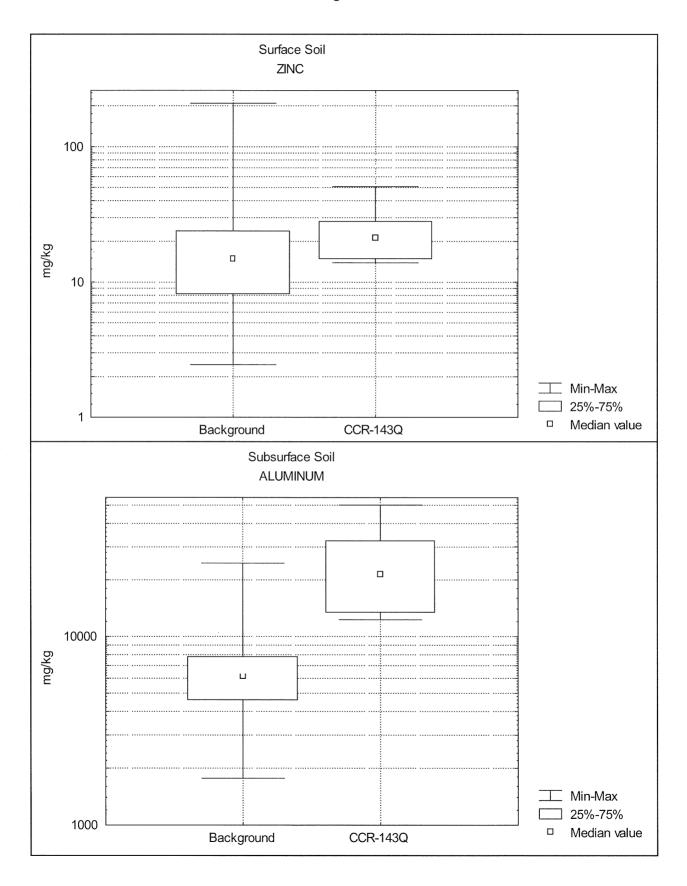


Figure 1-7

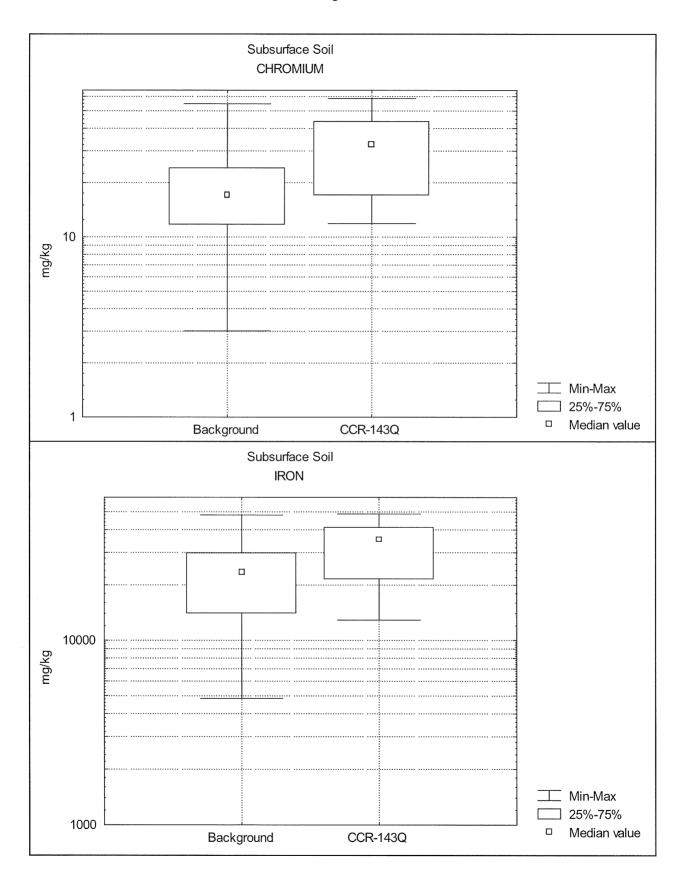


Figure 1-8

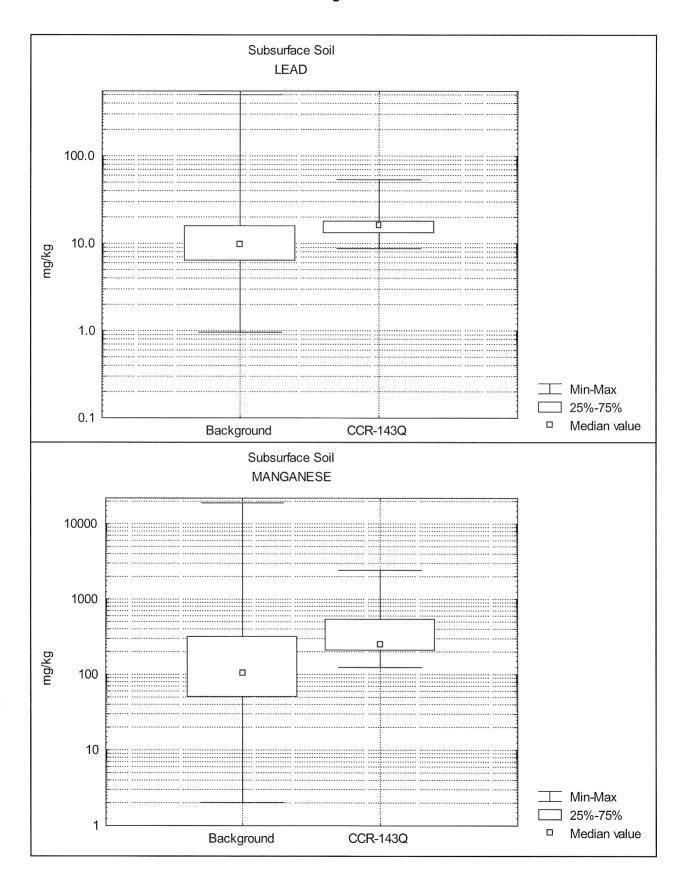


Figure 1-9

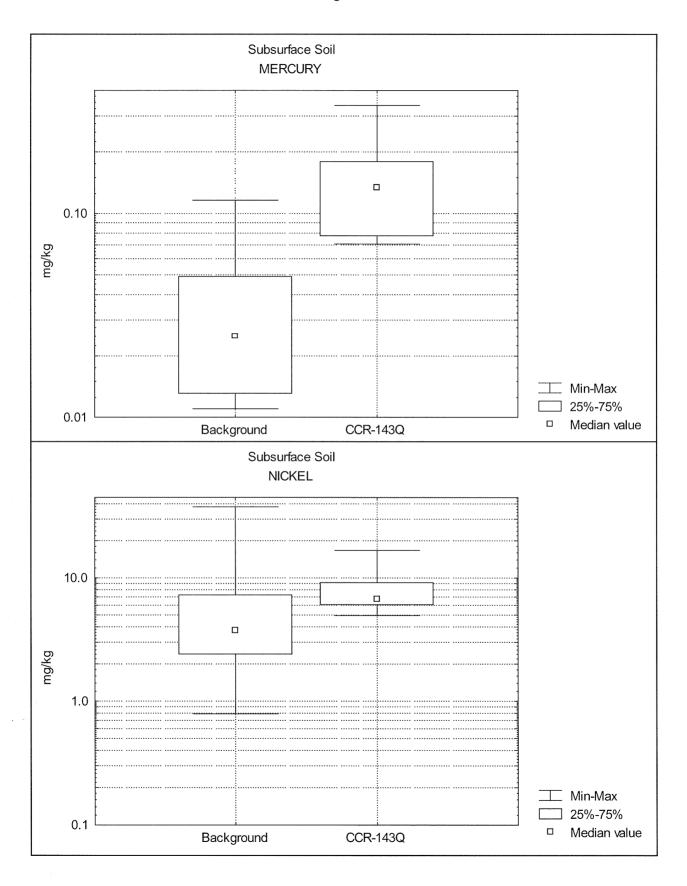


Figure 1-10

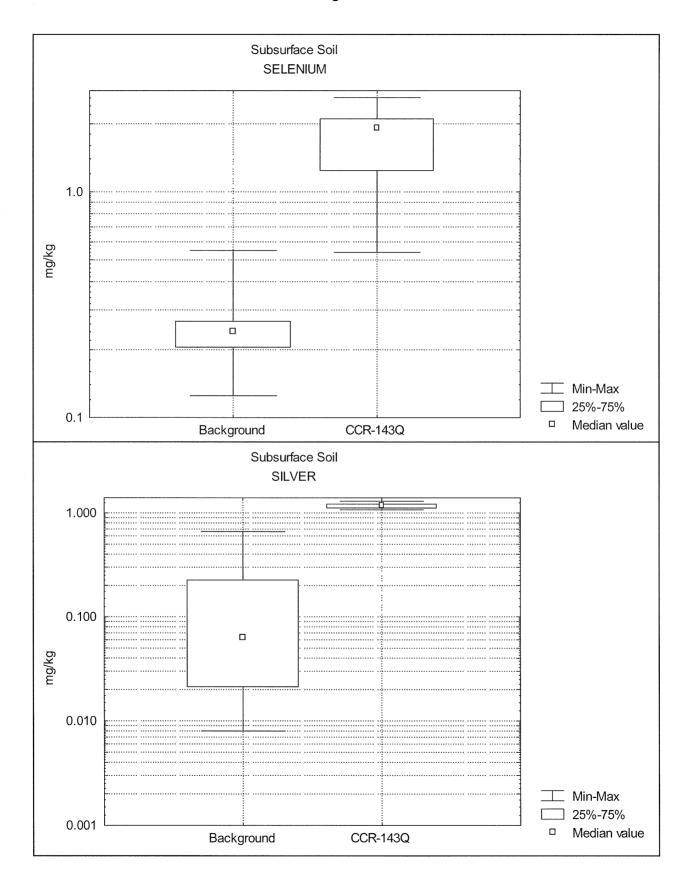


Figure 1-11

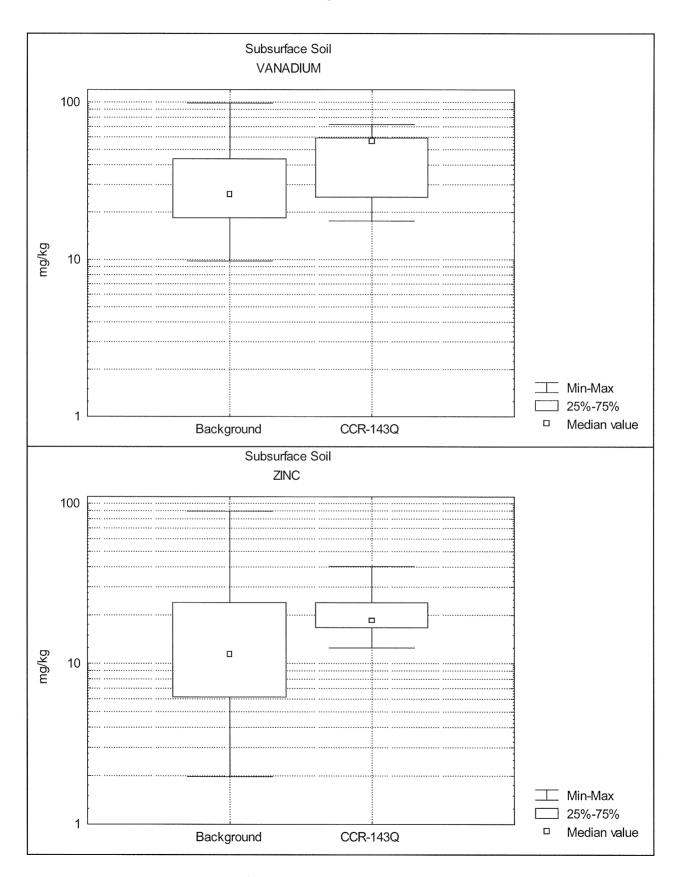
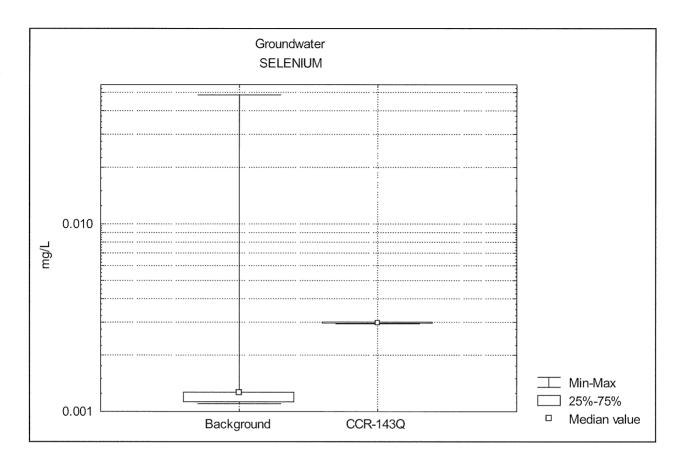


Figure 1-12



GEOCHEMICAL (TIER 3)

# Geochemical Evaluation of Metals in Soil Range, Choccolocco Corridor, Parcel 143Q Fort McClellan, Alabama

## 1.0 Introduction

This report provides the results of a geochemical evaluation of soil samples from the Range, Choccolocco Corridor, Parcel 143Q, at Fort McClellan in Calhoun County, Alabama. Fourteen elements in soil failed statistical comparison to background. A geochemical evaluation was performed to determine if the elevated concentrations are naturally occurring or if they contain a component of contamination.

Site samples included in the evaluation consist of 11 surface soil samples (obtained from a depth of 0 to 1 foot below ground surface [bgs]) collected in August 2002 and 8 subsurface soil samples (3 to 4 feet bgs) collected in August 2002. All of the site samples were analyzed for the full list of 23 target analyte list (TAL) metals. Installation-wide background data for TAL metals in soil are provided in the background study report (Science Applications International Corporation, 1998) and are used in the following evaluations.

# 2.0 Geochemical Evaluation Methodology

If an analyte fails statistical comparison to background as described in the "Statistical Comparison of Site and Background Data, Range, Choccolocco Corridor, Parcel 143Q," then a geochemical evaluation is performed to determine if the elevated concentrations are caused by natural processes. The importance of geochemical evaluations in distinguishing between site and background data sets has been recognized in the industry (EPA, 1995; Barclift, *et al.*, 2000; U.S. Navy, 2002; Myers and Thorbjornsen, 2004). When properly evaluated, geochemistry can provide mechanistic explanations for apparently high, yet naturally occurring, constituents. Anomalous samples that may represent contamination can also be readily distinguished from uncontaminated samples. This section describes the geochemical evaluation techniques that were employed in the Parcel 143Q site-to-background comparisons.

**Soil and Sediment.** The geochemical evaluation is based on the natural associations of trace elements with specific minerals in the soil or sediment matrix. As an example, arsenic in most uncontaminated oxic soils is almost exclusively associated with iron oxide minerals (Bowell, 1994; Schiff and Weisberg, 1997). (The term "iron oxide" is used here to include oxides, hydroxides, oxyhydroxides, and hydrous oxides of iron.) This association of arsenic with iron

oxides is a result of the adsorptive behavior of this particular trace metal in an oxic soil environment. Arsenic is present in oxic soil pore fluid as negatively charged oxyanions (HAsO<sub>4</sub><sup>-2</sup>, H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>) (Brookins, 1988). These anions have strong affinities to adsorb on the surfaces of iron oxides, which maintain a strong positive surface charge (Electric Power Research Institute [EPRI], 1986). If a soil sample has a high percentage of iron oxides, then it is expected to have a proportionally higher concentration of arsenic.

The absolute concentrations of arsenic and iron can vary by several orders of magnitude at a site, but the arsenic/iron ratios in the samples are usually quite constant as long as no contamination is present (Daskalakis and O'Connor, 1995). If a sample has some naturally occurring arsenic plus additional arsenic from an herbicide or some other source, then it will have an anomalously high ratio relative to the other uncontaminated samples. These ratios thus serve as a powerful technique for identifying contaminated samples.

The evaluation includes the generation of plots in which detected arsenic concentrations in a set of samples are plotted on the y-axis, and the corresponding detected iron concentrations are plotted on the x-axis. The slope of a best-fit line through the samples is equal to the average arsenic-to-iron background ratio. If the samples with the highest arsenic concentrations plot on the same linear trend as the other samples, then it is most probable that the elevated concentrations are natural, and are caused by the preferential enrichment of iron oxides in those samples. If the site samples with elevated arsenic concentrations plot above the trend displayed by the uncontaminated samples, then there is evidence that those samples have an excess contribution of arsenic, and contamination may be indicated.

Each trace element is associated with one or more minerals in the soil matrix. Vanadium and selenium, along with arsenic, form anionic species in solution and are associated with iron oxides, which maintain a positive surface charge. Divalent metals such as barium, cadmium, lead, and zinc tend to form cationic species in solution and are attracted to clay mineral surfaces, which maintain a negative surface charge. These trace elements would be evaluated against aluminum, which is a major component of clay minerals. Manganese oxides also have an affinity to adsorb divalent cations such as barium, cobalt, and lead (Kabata-Pendias, 2001). These trace elements would be evaluated against manganese.

# 3.0 Results of the Geochemical Evaluation for Multiple Elements in Soil

This section presents the results of the geochemical evaluation of aluminum, barium, beryllium, chromium, iron, lead, manganese, mercury, nickel, potassium, selenium, silver, vanadium, and zinc in soil samples from Parcel 143Q. Correlation plots are provided in Attachment 1.

#### **Aluminum**

The Parcel 143Q soil boring logs note the presence of clays in many of the sampled intervals. Aluminum is a primary component of common soil-forming minerals such as clays, feldspars, and micas. Iron oxides are minerals that are also common in soil. Clays and iron oxides tend to exist as very fine particles, so both aluminum and iron are enriched in samples with finer grain sizes. A plot of aluminum versus iron concentrations can be used to qualitatively assess the relative abundance of these minerals in site soil (Figure 1). Site surface soil samples are represented by open triangles, site subsurface soil samples by filled triangles, and background soil samples by filled circles. The site samples generally exhibit higher aluminum concentrations than most of the background samples, but they contain proportionally higher iron and lie on the background trend. This indicates that aluminum in the site samples is naturally occurring. It is worth noting that iron oxide and clay minerals adsorb specific trace elements (as discussed in Section 2.0), so the samples that plot on the upper end of the trend in Figure 1 are expected to contain proportionally higher concentrations of trace elements.

#### Conclusion

Aluminum detected in the site soil samples is naturally occurring.

#### **Barium**

Manganese oxides have a strong affinity to adsorb divalent metals such as barium, cobalt, and lead (Kabata-Pendias, 2001). If a soil sample contains a high proportion of manganese oxides, then it is expected to contain high concentrations of manganese and associated trace elements. The site and background samples form a collinear trend in a plot of barium versus manganese (Figure 2). The site samples with high barium concentrations also contain proportionally higher manganese, and lie on the trend established by the other samples. These observations indicate that the barium detected in the site samples is natural.

## Conclusion

Barium concentrations detected in the site soil samples are naturally occurring.

#### Beryllium

A plot of beryllium versus manganese is provided in Figure 3. The site samples form a common linear trend with the background samples ( $R^2 = 0.57$  and 0.99 for the site surface and subsurface intervals). The site samples that have the highest beryllium concentrations also have the highest manganese, and lie on the linear trend. This indicates that beryllium in the site samples is associated with manganese oxides at a relatively constant ratio, and is natural.

Beryllium detected in the site soil samples is naturally occurring.

## Chromium

Chromium has an affinity to adsorb on iron oxides (Cornell and Schwertmann, 1996). The site and background samples form a common linear trend with a positive slope in a plot of chromium versus iron (Figure 4). The site samples with the highest chromium concentrations contain proportionally higher iron and lie on the trend established by the other samples. Chromium in the samples is associated with iron oxides at a relatively constant ratio, and is natural.

## Conclusion

Chromium concentrations detected in the site soil samples are naturally occurring.

#### Iron

As discussed in the Aluminum evaluation, iron oxides and clays are common soil-forming minerals and tend to concentrate specific trace elements. The plot of aluminum versus iron provides a qualitative indicator of the relative abundance of these minerals in site soil (Figure 1). The site samples generally exhibit a range of iron concentrations that is similar to background, and they lie on the background trend. This indicates that iron in the site samples is naturally occurring. It is important to note that iron oxides and clays adsorb specific trace elements (as discussed in Section 2.0), so the samples that plot on the upper end of the trend in Figure 1 are expected to contain proportionally higher concentrations of trace elements.

## Conclusion

Iron detected in the site soil samples is naturally occurring.

#### Lead

Manganese oxides in soil have a strong affinity to adsorb divalent cations such as barium, cobalt, and lead (Kabata-Pendias, 2001). Samples that contain a high percentage of manganese oxides will contain elevated manganese concentrations and proportionally higher lead. A common linear trend with a positive slope is observed for the site and background samples in a plot of lead versus manganese ( $R^2 = 0.66$  and 0.93 for the site surface and subsurface intervals) (Figure 5). The site samples with high lead also have high manganese, and lie on the linear trend. This indicates that lead in the site samples is associated with manganese oxides at a relatively constant ratio, and is natural.

#### Conclusion

Lead concentrations detected in the site soil samples are naturally occurring.

## Manganese

As discussed previously, manganese oxides are common in soil and have an affinity to adsorb specific trace elements such as barium, cobalt, and lead. A positive correlation is thus expected between manganese and associated trace elements in uncontaminated soil samples. The positive correlations observed for barium vs. manganese and lead vs. manganese, and the absence of outliers plotting off the linear trends on the correlation plots, indicate a natural source for these two elements (Figures 2 and 5).

Manganese in the site soil samples is naturally occurring.

## Mercury

Mercury concentrations in soil are commonly controlled through organic complex formation (Kabata-Pendias, 2001), so poor correlations between mercury and iron or mercury and aluminum are often observed, even in uncontaminated soil samples. A plot of mercury versus aluminum is provided in Figure 6. The site samples with high mercury also have high aluminum, and all of the site samples lie on the general background trend. These observations indicate a natural source for mercury in the site samples.

## Conclusion

Mercury concentrations detected in the site soil samples are naturally occurring.

#### **Nickel**

Nickel is commonly associated with clays in soils (Kabata-Pendias, 2001). A plot of nickel versus aluminum reveals a linear trend with a positive slope for the site samples and many of the background samples ( $R^2 = 0.85$  and 0.79 for the site surface and subsurface intervals) (Figure 7). The site samples with high nickel also contain proportionally higher aluminum, and lie on the linear trend. This indicates that nickel in the site samples is associated with clays at a relatively constant ratio, and is natural.

## Conclusion

Nickel concentrations detected in the site soil samples are naturally occurring.

#### **Potassium**

Potassium is a major element that is a common constituent of minerals such as clays, which also contain aluminum. A plot of potassium versus aluminum reveals a linear trend for many of the background samples (Figure 8). The site samples have higher potassium concentrations than some of the background samples, but they also have higher aluminum and lie on the linear trend. Potassium in the site samples is associated with clays and other aluminum-bearing minerals at a relatively constant ratio, and is natural.

#### Conclusion

Potassium detected in the site soil samples is naturally occurring.

## Selenium

As explained in Section 2.0, selenium has a strong affinity to adsorb on iron oxides in oxic soils, so a positive correlation between selenium and iron is expected for uncontaminated soil samples. Comparison to background is hindered because of the high percentage of nondetects in the background data set. However, a plot of selenium versus iron reveals a strong linear trend with a positive slope for the site samples ( $R^2 = 0.80$  and 0.89 for the site surface and subsurface intervals) (Figure 9). The site samples with the highest selenium concentrations also exhibit high iron content, and lie on the linear trend. Selenium in the samples is associated with iron oxides at a relatively constant ratio, and is natural.

Selenium detected in the site soil samples is naturally occurring.

## Silver

A plot of silver versus aluminum is provided in Figure 10. The single site sample with detectable silver has a higher concentration most of the background samples, but it also has the highest aluminum concentration. This suggests that the sample is preferentially enriched in clay minerals and associated trace elements, and that the silver is natural. It is important to note that the site detection is an estimated value (1.3 J mg/kg) below the reporting limit, and that such values are highly uncertain. In comparison, the background detections are mostly unestimated concentrations ranging from 0.019 to 1.87 mg/kg, with a mean of 0.128 mg/kg (14 of the 82 background samples are estimated values). Additionally, the site samples are characterized by higher reporting limits relative to the background samples: the site reporting limits range from 2.09 to 2.51 mg/kg, with a mean of 2.25 mg/kg, whereas the reporting limits for the background nondetects range from 0.016 to 1.2 mg/kg, with a mean of 0.293 mg/kg [reporting limit data are unavailable for the background detected concentrations]. The uncertainty associated with the estimated site concentrations, combined with the difference in reporting limits between the data sets, may explain why the site sample does not exhibit the same Ag/Al ratio exhibited by the background samples.

## Conclusion

The single detected concentration of silver is observed in a soil sample with high aluminum content, and is natural.

## Vanadium

As discussed in Section 2.0, vanadium is present in oxic soils as oxyanions, which have a strong affinity to adsorb on iron oxides. A positive correlation between vanadium and iron is thus expected for uncontaminated samples. A plot of vanadium versus iron is provided in Figure 11. The site and background samples form a strong collinear trend ( $R^2 = 0.95$  and 0.94 for the site surface and subsurface intervals). The site samples with the highest vanadium also contain the highest iron, and lie on the linear trend. Vanadium in the site samples is associated with iron oxides at a nearly constant ratio, and is natural.

#### Conclusion

Vanadium detected in the site samples is naturally occurring.

## **Zinc**

Zinc commonly substitutes for magnesium in silicate minerals (Kabata-Pendias, 2001), so a positive correlation between zinc and magnesium concentrations is often observed for uncontaminated soil samples. The site and background samples form a common linear trend in a plot of zinc versus magnesium ( $R^2 = 0.91$  and 0.53 for the site surface and subsurface intervals, respectively) (Figure 12). The samples with high zinc also contain high magnesium, and lie on the background trend. These observations indicate that zinc in the site samples is associated with magnesium-bearing minerals at a relatively constant ratio, and is natural.

Zinc detected in the site soil samples is naturally occurring.

## 4.0 Summary

Geochemical evaluation indicates that all of the aluminum, barium, beryllium, chromium, iron, lead, manganese, mercury, nickel, potassium, selenium, silver, vanadium, and zinc concentrations detected in the Parcel 143Q surface and subsurface soil samples are naturally occurring. The available data do not indicate inorganics contamination in the site samples.

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